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NITRATION AND HIGH ENERGY NITROGEN COMPOUNDS. (U)  
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Electrophilic nitration, regioselectivity, substrate selectivity,  $\pi$ -complex/encounter pair, diarylchloronium ions, diarylbromonium ions, nucleophilic nitrolysis, o-nitration, nitrate esters, transfer nitration, ambident reactivity, nitronium(nitracidium) ions,  $^{13}\text{C}$ ,  $^{15}\text{N}$  and  $^{31}\text{P}$  NMR.

Electrophilic nitration of aromatics with a wide variety of nitrating systems were carried out to elucidate the general mechanism of the reaction. The study with reactive nitrating agents clearly reinforce our earlier view that substrate and positional selectivity are determined in two separate steps. Studies on the nitration of naphthalene show that the suggested radical cation pair mechanism is not of general importance. The reversibility of electrophilic aromatic nitration was demonstrated using superacid catalysts.

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20. (continued)

Transfer nitrations were carried out with various transfer nitrating agents including preparation of nitrate esters of polyols. Solid superacid catalyzed nitration of aromatics with various nitrating agents was developed. The ambident reactivity of nitronium ion was demonstrated in the reaction of sulfides, selenides and phosphines using  $^{13}\text{C}$ ,  $^{15}\text{N}$  and  $^{31}\text{P}$  NMR spectroscopy.

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Summary Research Report: July 15, 1977 - October 14, 1980

Electrophilic nitration of toluene and benzene was studied under a variety of conditions with several nitrating systems. It was found that high ortho-para regioselectivity is prevalent in all reactions, and is independent of the reactivity of the nitrating agent. There is also no apparent correlation between reactivity of the reagent and selectivity of the nitrations. The methyl group of toluene is predominantly ortho-para directing under all reaction conditions. Steric factors are considered important, but not the sole reason for the variation in the ortho/para ratio. The results reinforce our earlier views, that in electrophilic aromatic nitrations with reactive nitrating agents, substrate and positional selectivities are determined in two separate steps. The first step involves a transition state of  $\pi$ -aromatic- $\text{NO}_2^+$  ion complex or encounter pair nature, whereas the subsequent step is of arenium ion nature (separate for the ortho, meta, and para position). The former determines substrate selectivity, whereas the latter determines regioselectivity. Thermal free radical nitration of benzene and toluene with tetranitromethane in sharp contrast gave nearly statistical product distributions.

The nitration of toluene and anisole was studied with nitrating systems of varying reactivity. High regioselectivity of ortho-para over meta substitution was maintained in all nitrations, regardless of the reactivity of the nitrating system. At the same time, the amount of meta substitution stayed low (3% or less), even when the fast reactions may have reached the encounter controlled limit. As the nitration of o-xylene, in which case both of the ring positions are activated by the effect of a methyl group, also does not show any diminishing of regioselectivity, the possibility of a dual mechanistic pathway, in which the activated position would react by a fast, encounter controlled path, whereas the non-activated meta position by a slower  $\sigma$ -type path, can be ruled out. Data unambiguously prove that the high regioselectivity of electrophilic aromatic nitration is independent of the reactivity of the reagent,

as no significant increase of meta substitution of toluene or anisole is observed regardless of the activity of the nitrating system. No selectivity-reactivity relationship is thus evident and the ortho-para directing effect of primary substituents over meta substitution is always maintained with the isomer distributions varying significantly depending on the nitration. The variation of the meta isomer upto the observed limit of about 3% in the case of toluene, and <2% for anisole, although probably significant, but cannot be, at the present time, quantitatively evaluated with the  $\pm 0.5\%$  overall reproducible accuracy of the isomer distributions of nitrations. Steric factors, such as increasing bulkiness of the nitrating agent, also can effect the ortho-para isomer ratios, but are not considered to be the only reason for the observed variations, which reflect the nature and reactivity of the nitrating systems, effecting the nature and position of the transition state of highest energy on the reaction pathway. Clearly, in nitrations with strongly electrophilic nitrating systems, there are two distinct intermediates involved, separated by a transition state. The latter is of arenium ion nature and determines regioselectivity. The former is a  $\pi$ -aromatic- $\text{NO}_2^+$  ion complex/or encounter pair, which determines overall rates/substrate selectivity. The original Ingold mechanism thus must be modified to accommodate two separate distinct steps leading to  $\sigma$ -intermediates.

An improved method of preparation of diarylchloronium and diarylbromonium ions from their corresponding arenediazonium ions by decomposition in haloarenes in the presence of trifluoro (trichloro) acetic acid or 2,2,2-trifluoroethyl alcohol was worked out.  $^{13}\text{C}$  nmr spectroscopic study of the prepared halonium ions shows that nearly equal amount of charge is transmitted into the two aryl rings regardless of the methyl substitution in one or both rings, suggesting that ring delocalized canonical structures are only limited resonance contributors. The potential utility of symmetrical and unsymmetrical diarylchloronium, -bromonium and -iodonium ions in their nucleophilic nitrolysis with sodium nitrite giving nitroarenes was studied.

The relative reactivity of the 4-tolyl, phenyl, 3-tolyl salts has been established as 1.0, 3.0, 3.6 and 14.1, respectively. Substitution of tetraphenylborate for hexafluorophosphate as counter ion did not affect the product distribution in the nitration reaction. The data obtained are best accommodated by an  $S_N2$ -like mechanism controlling the collapse of ionic diarylchloronium nitrites initially formed by displacement of the corresponding counter ion to give nitro- and chlorobenzene derivatives.

Alcohols and polyols can be converted into the corresponding nitrate esters by the O-nitration with either mixed nitric-sulfuric acid, nitronium tetrafluoroborate, or acetyl nitrate. Nitrate esters can be obtained by metathesis of the corresponding alkyl halides with silver nitrate. The first three methods involve acidic conditions with frequently elaborate safety precautions, whereas the last method uses an equimolar amount of the silver salt. Moreover, presence of even very small amounts of nitrite ion give highly unstable nitrite esters. A recently published procedure claims to involve less hazards. It uses, however, highly acidic conditions with a strong oxidizing agent in contact with an organic solvent. Such mixture of reagents is known to be potentially very dangerous. We have previously shown the efficiency of N-nitropyridinium salts for transfer nitration reactions. We have developed an improved mild procedure for the preparation of alkyl nitrates via transfer nitration of the corresponding alcohols (as well as polyols) with N-nitrocollidinium tetrafluoroborate.

Significant new results were obtained in carrying out electrophilic aromatic nitrations over solid superacidic catalysts, such as the H-form of Nafion, a perfluorinated sulfonic acid resin. The acidity of this solid acid catalyst exceeds that of sulfuric acid and allows efficient nitrations to be carried out with various nitrating agents without the use of a liquid acid system (such as sulfuric acid). There is no need of aqueous-caustic work up or acid disposal. Obvious advantages are foreseen for a wide variety of applications.

The reversibility of electrophilic aromatic nitration was proven in superacid catalyzed transfer nitration of benzene, toluene and mesitylene with 9-nitro-anthracene and pentamethyl nitrobenzene.

Studies were carried out on the mechanism of the nitration of naphthalene showing that Perrin's suggested radical cation pair mechanism is not of general significance.

The reaction of nitronium salts with sulfides, selenides, phosphines, arsines, and stibines has been investigated. Nitronium hexafluorophosphate (tetrafluoroborate) reacts rapidly at  $-78^{\circ}\text{C}$  with diaryl, arylalkyl and dialkyl sulfides, affording sulfoxides as the major products. Selenides, phosphines, arsines, and stibines react equally readily, giving the corresponding oxygenated products. In the case of diphenyl sulfide, less than 5% of the competing ring C-nitro products were obtained. These observations suggest the intermediacy of nitrito onium ions ( $>\text{X}^{+} \cdots \text{ONO}$ ) being in equilibrium with the related nitro onium ions ( $>\text{X}^{+} \cdots \text{NO}_2$ ).

This study represents the first demonstration of the ambident reactivity of the nitronium ion in solution chemistry (i.e. competing attack on oxygen vs. nitrogen of  $\text{NO}_2^{+}$ ). The equilibrium was confirmed by carrying out trans-nitrosation of N,N-dimethyl aniline in the presence of these onium salts.  $^{13}\text{C}$ ,  $^{15}\text{N}$  and  $^{31}\text{P}$  NMR studies of the onium salts are also reported, showing that nitro onium salts are irreversible transformed into nitrito onium salts either upon raising the temperature or during prolonged reaction times.

The transfer nitration of aromatics with various N-nitropyridinium and quinolinium salts ( $\text{PF}_6^{-}$  or  $\text{BF}_4^{-}$ ) was studied. The nitrations were found to take place via a nucleophilic displacement pathway, involving the N-nitropyridinium ions themselves and not free nitronium ion. Steric factors were, however, shown to play an insignificant role in determining the positional selectivity of nitration. Positional and substrate selectivities were found to be independent of one another and are suggested to be determined in two separate steps.

The nature of the ionic intermediates formed by the protonation, methylation or Lewis acid fluoride complexation of aliphatic and aromatic nitrocompounds was investigated by low temperature (-40 to 100°C)  $^{13}\text{C}$  NMR spectroscopy. Protonation and methylation of the nitrocompounds were carried out in  $\text{FSO}_3\text{H}:\text{SbF}_5$  (1:1)/ $\text{SO}_2\text{ClF}$  and  $\text{CH}_3\text{F}:\text{SbF}_5/\text{SO}_2$ , respectively, whereas complexations were studied with  $\text{BF}_3$  and  $\text{SbF}_5$  in the same solvents. In all cases, the electrophiles interact with only one of the oxygen atoms of the nitro group. In order to assess the  $^{13}\text{C}$  NMR chemical shift and the coupling constants of the nitronium ions obtained, they were compared to the chemical shifts of the corresponding parent (neutral) nitro compounds. Whereas appreciable deshielding was observed for the  $\alpha$ -carbons in aliphatic nitro compounds, slight shielding was found for the carbons directly attached to the nitro group (ipso carbon) in aromatic nitro compounds. The origin of these effects was evaluated in the studied nitronium (nitracidium) ions. These ionic complexes are of significance under the electrophilic conditions of nitration reactions.

The facile conversion of nitro into carbonyl compounds with hydrogen peroxide/potassium carbonate was studied, as a useful preparative utilization of nitrocompounds.

A comprehensive review article on our work on aromatic nitration was prepared.



List of Publications under ARO Sponsorship

Olah, George A., Lin, Henry C., Olah, Judith A., and Narang, Subhash C. Aromatic Substitution. 41. "Variation of the Isomer Distribution in the Electrophilic Nitration of Toluene, Anisole and Ortho-Xylene. The Independence of High Regioselectivity from the Reactivity of the Reagent", Proc.Natl.Acad.Sci., 75, 545 (1978).

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